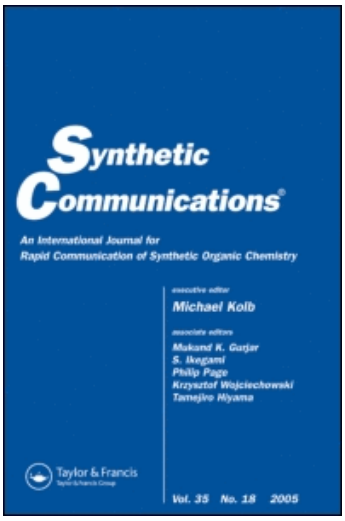

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A New Method for the Esterification of Sulphonic Acids

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A NEW METHOD FOR THE ESTERIFICATION OF SULPHONIC ACIDS

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Abstract

Sulphonic acids can be smoothly converted to their methyl and ethyl esters by reaction with trimethyl and triethyl orthoformate, respectively.

In connection with our continuing studies directed towards the elucidation of lignin sulphonate structures[1,2], we wish to report new methodology for the facile methylation (and ethylation) of sulphonic acids with trimethyl (and triethyl) orthoformate respectively.

Currently, the only means of converting sulphonated lignin fragments into stable, organic soluble derivatives, under relatively mild conditions, is to prepare their a) S-benzylthiourea salts[3] or b) acetyl lignin sulphonate methyl esters[4]. This latter method, requiring initial acetylation of a suspension of lignin sulphonates in acetic anhydride/pyridine, and subsequent methylation of the silver salt of the sulphonic acid with methyl iodide, is somewhat tedious.

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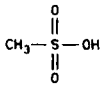
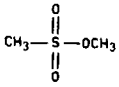
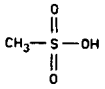
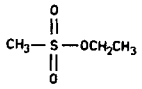
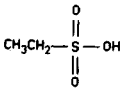
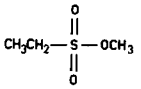
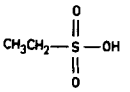
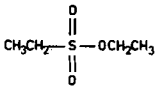
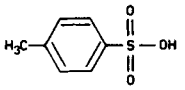
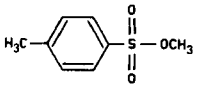
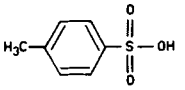
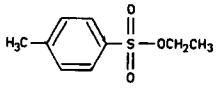
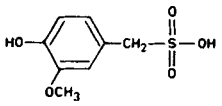
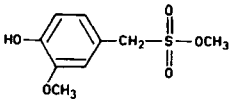
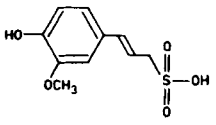
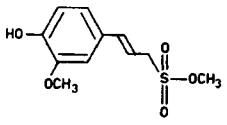
Methyl sulphonates[5] and methyl sulphinates[6] can be readily prepared by the treatment of the corresponding acid with diazomethane. However, with sulphonated lignin model compounds e.g. 5 (Table 1) alkylation of both phenolic and sulphonic acid functionalities occur[2]. Since we were interested in the selective alkylation of the sulphonic acid group, we turned our attention to other methods.

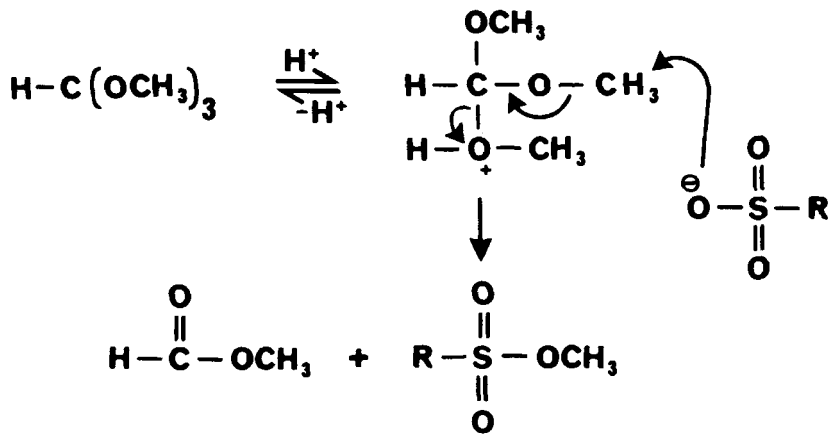
Previously, it had been reported[7] that carboxylic acids can be efficiently converted to their esters by the simple treatment of an alcoholic solution of the acid with 2.5 equivalents of trimethylsilylchloride (TMSiCl). Unfortunately, even in the simplest case (p-toluenesulphonic acid), esterification with methanol and TMSiCl gave only unreacted starting material, as evidenced by ^1H n.m.r. and infrared spectroscopy.

We therefore addressed the action of trimethyl orthoformate on p-toluenesulphonic acid, since the former has been used successfully for both acid-catalysed ketalisations[8,9] and esterification of carboxylic acids[10,11]. Thus, when acid 3 (see Table 1) was allowed to stand in excess trimethyl orthoformate (17 equivalents) for 14 h. at room temperature, a quantitative yield of methyl p-toluenesulphonate was obtained. In a similar fashion, triethyl orthoformate gave the corresponding ethyl ester. The general applicability of this method can be seen from Table 1. Each of the reactions gave a single product in high yield, unless it was very volatile and then recovery was lower. Note also that

Table 1: Alkylation of Sulphonic Acids with Trimethyl or Triethyl Orthoformate

	Sulphonic Acid	Reagent	Product	Yield (%)
1		$HC(OCH_3)_3$		43*
		$HC(OCH_2CH_3)_3$		80*
2		$HC(OCH_3)_3$		83*
		$HC(OCH_2CH_3)_3$		73*
3		$HC(OCH_3)_3$		99
		$HC(OCH_2CH_3)_3$		98
4		$HC(OCH_3)_3$		85
5		$HC(OCH_3)_3$		82

* Yield low due to volatility of product



R = alkyl, aryl, benzyl

Scheme 1

in the case of sulphonic acids 4 and 5, containing free phenolic groups, only the acid functionality was alkylated.

Scheme 1 represents a possible pathway for the formation of these products.

For non-volatile products, the alkylation could also be carried out by heating to reflux, e.g., the acid 3 with trimethyl orthoformate for 30 min.

Further, since paucidisperse lignosulphonic acids can be dissolved in methanolic solution[2], we have investigated the use of the alkylating agent in methanol. Thus, 3 was smoothly converted to methyl p-toluenesulphonate using a 1:1 solution of methanol :

trimethyl orthoformate, and slowly distilling off the methanol over a period of 1 h.

General Procedure

A solution of the sulphonic acid (200 mg.) in trimethyl (or triethyl) orthoformate (2 mL) was either allowed to stir at room temperature for 14 h., or heated to reflux for 30 min., under an atmosphere of nitrogen. The excess orthoformate was then removed under vacuum (0.5 mm. Hg) to give the corresponding methyl (or ethyl) ester. Where the solubility of the substrate was poor, the reagent was mixed with an equal volume of methanol, following which slow distillation over 1 h. gave the required ester in high yield.

Acknowledgements

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References

1. LEWIS, N.G., GORING, D.A.I. and WONG, A., Can. J. Chem., 1983, 61, 416.
2. FONG, J.L., LEWIS, N.G. and LUTHE, C.E. (manuscript submitted to Can. J. Chem.).
3. SCHUBERT, S.W., ANDRUS, M.G., LUDWIG, C., GLENNIE, D. and McCARTHY, J.L., Tappi, 1967, 50(4), 186.
4. COLLINS, J.J., FORSS, K., GLASSER, W.G., GRATZL, J.S. and McCARTHY, J.L., Macromolecules, 1975, 8(5), 565.
5. TORO, P., Bol. Soc. Chil. Quim., 1981, 26, 59.
6. MEEK, J.S. and FOWLER, J.S., J. Org. Chem., 1968, 33, 3422.

7. BROOK, M.A. and CHAN, T.H., Synthesis, 1983, 201.

8. CARSWELL, H.E. and ADKINS, H., J. Am. Chem. Soc., 1928, 50, 235.

9. PFEIFFER, G.J. and ADKINS, H., ibid., 1931, 53, 1043.

10. COHEN, H. and MIER, J.D., Chem. and Ind. (London), 1965, 349.

11. BLUME, R.C., Tetrahedron Lett., 1969, 1047.